

PTO 10-1035

DE
19860724
A1
3501697

RUBBER MIXTURES AND THEIR COVULCANIZATES
[Kautschukmischungen und ihre Covulkanisate]

Dieter Brück et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. DECEMBER 2009
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY (19): DE

DOCUMENT NUMBER (11): 3501697

DOCUMENT KIND (12): A1

PUBLICATION DATE (43): 19860724

APPLICATION NUMBER (21): P3501697.3

APPLICATION DATE (22): 19850119

INTERNATIONAL CLASSIFICATION⁴ (51): C 08 L 9/02
C 08 L 23/16
C 08 J 3/24

INVENTORS (72): Dieter Brück et al.

APPLICANT (71): Bayer AG

TITLE (54): RUBBER MIXTURES AND THEIR COVULCANIZATES

FOREIGN TITLE [54A]: Kautschukmischungen und ihre Covulkanisate

1. Rubber mixtures of (1) 5-50 wt%, with respect to the total amount of polymer, of a butadiene-acrylonitrile copolymer with an acrylonitrile content from 13-24 wt% and a Mooney value of 25-100, (2) 75-30 wt%, with respect to the total amount of polymer, of a butadiene-acrylonitrile copolymer with an acrylonitrile content from 32-48 wt% and a Mooney value from 25-100, and (3) 20-50 wt%, with respect to the total amount of polymer, of an ethylene-propylene-diene copolymer with a propylene content of 10-50 wt%, a diene content of 5-16 wt%, and a Mooney value from 50-140, where the diene is ethylenenorbornene or 1,4-hexadiene.
2. Rubber mixtures as in Claim 1, where (1) has an acrylonitrile content of 15-20 wt% and (2) has an acrylonitrile content of 37-45 wt% and a Mooney value of 50-90.
3. Rubber mixtures as in Claim 1, of 10-30 wt% (1), 60-40 wt% (2) and 30-50 wt% (3).
4. Rubber mixtures as in Claim 1, where (3) has an ethylene content greater than 65 wt%.
5. Covulcanizates of the rubber mixtures as in Claims 1-4.

^{*} [Numbers in right margin indicate pagination of the original text.]

The invention concerns rubber mixtures of nitrile rubber (NBR) and ethylene-propylene terpolymer rubber (EPDM) and the covulcanizates produced from them by vulcanization. /2

EPDM/NBR blends are known, for example, from Rubber Chem. Techn. 44, 1065-1079 (1971), US-PS 3 646 168, DE-OS 2 532 115 and FR-PS 1 555 597. These blends have many applications and show attractive property combinations of ozone resistance, oil resistance and good high- and low-temperature properties.

A disadvantage is the insufficient strength of molded objects made of such vulcanized blends, which is not only lower than the strength of the NBR, but also lower than the strength of the EPDM, which is even poorer than NBR in this regard. This disadvantage can be somewhat ameliorated according to the prior art only by a drastic increase of the diene content in the EPDM or by special vulcanization accelerators.

In conventional systems this failure had not been remedied even in 1977 (Gummi, Asbest, Kautschuk 30, 8/1977, pp. 498-504). /3

The task of the invention was to make available EPDM/NBR blends that, besides the required properties of ozone resistance, oil resistance and good high- and low-temperature properties, show good strength and dynamic lifespan.

The task is solved in accordance with the invention by the fact that an EPDM type that contains ethylenenorbornene or 1,4-hexadiene as the diene is mixed in specific amounts with at least two types of NBR that have different nitrile contents.

The object of the invention therefore consists of rubber blends of (1) 5-50 wt%, with respect to the total amount of polymer, of a butadiene-acrylonitrile polymer with an acrylonitrile content of 13-24, preferably 15-20 wt%, and a Mooney value of 25-100, (2) 75-30 wt%, with respect to the total amount of polymer, of a butadiene-acrylonitrile polymer with an acrylonitrile content of

32-48, preferably 37-45 wt% and a Mooney value of 25-100, preferably 50-90, and (3) 20-50 wt%, with respect to the total amount of polymer, of an ethylene-propylene-diene copolymer with a propylene content of 10-50 wt%, a diene content of 5-16 wt% and a Mooney value of 50-140, where the diene is ethylenenorbornene or 1,4-hexadiene.

Preferably the blend contains 10-30 wt% (1), 60-40 wt% (2) and 30-50 wt% (3), where in particular EPDM copolymers with Mooney values >80 and diene contents >8 wt% or EPDM copolymers with ethylene contents >65 wt% are used.

The blends can contain the usual blending components, which are known to the specialist. These are, for example, fillers, plasticizers, antioxidation agents, processing aids, pigments, acid acceptors and vulcanization chemicals, where chiefly sulfur or sulfur donors are used for the vulcanization of the rubber blends in accordance with the invention.

Sulfur is used in amounts of 0.1-5, preferably 0.1-1.8 wt%, with respect to the polymer, while sulfur donors are used in amounts of 0.2-8, preferably 2-4 wt%, with respect to the polymer.

Suitable sulfur donors are, for example, tetraalkylthiuram disulfides, cycloalkylalkylthiuram disulfides, arylalkylthiuram disulfides, tetraalkylthiuram tetrasulfides or morpholinyldithiobenzothiazole.

Another object of the invention consists of covulcanizates of the said blends, which are obtained preferably by sulfur vulcanization.

The covulcanizates have good low temperature properties, oil resistance, ozone resistances, abrasion resistance and resistance to dynamic loading. They are suitable, for example, as outer sheathing of hoses, outer layers of conveyor belts, or drive belts.

Example 1

/6

This example is intended to show that an NBR-EPDM blend has better strength and dynamic life span (De Mattia) if the NBR component was produced from two nitrile rubbers with different nitrile contents (data given in parts by weight).

	1	2
NBR I	17	-
NBR II	-	60
NBR III	43	-
EPDM I	40	40
Carbon black N 330	20	20
Carbon black N 762	60	60
ZnO	5	5
Ether thioether ¹⁾	10	10
Alkylsulfonic acid alkylphenyl ester ²⁾	10	10
Styrenated diphenylamine	2	2
Zinc salt of 4- or 5-methylmercaptobenzthiazole	3	3
Stearic acid	1	1
Ca stearate	1	1
Sulfur	1.8	1.8
Benzothiazyl-2-cyclohexyl sulfonamide	1.2	1.2

¹⁾ Vulkanol 85, Bayer AG, was used

²⁾ Vulkanol SF, Bayer AG, was used

NBR I had an acrylonitrile content of 18 wt% and a Mooney viscosity ML 1+4/100°C of 45
Mooney units (MU)

/7

NBR II had an acrylonitrile content of 34 wt% and a Mooney viscosity ML 1+4/100°C of 65 MU

NBR III had an acrylonitrile content of 39 wt% and a Mooney viscosity ML 1+4/100°C of 45 MU.

EPDM I contains 6 wt% 5-ethylidene-2-norbornene and 48 wt% ethylene. EPDM I is a statistical copolymer with rapid vulcanization characteristic and a Mooney viscosity ML 1+4/100°C of 45 MU.

	1	2
Density (g/cm ³)	1.198	1.202
Blend ML 1+4/100°C (MU)	55	58
Vulkameter 160°C		
t ₁₀	2.5	2.3
t ₉₀	14.0	17.9
Standard rod II (DIN) Vulcanization, 160°C, 25 min		
Tensile strength (MPa)	9.7	8.8
Breaking elongation (%)	190	160
Strain, 100% (MPa)	5.9	6.6
Hardness 23°C (Shore A)	72	75
Elasticity 23°C (%)	28	27
Brittle point (°C)	-36	-22

Long-term bending test, crack formation

Step 3 at 23°C (no. of bendings) 2.0 0.8
(De Mattia)

The DIN standards that were used were 53 504, 53 512, 53 505, 53 522.

Example 2

/8

This example is intended to show that an NBR-EPDM blend with an NBR component that contains two types of NBR, with a high viscosity, extremely fast vulcanizing EPDM type is even better when it has a high ethylene content (sequence type) (data in parts by weight).

	1	2	3	4	5	6
NBR I	17	17	17	17	17	17
NBR III	43	—	—	—	—	—
NBR IV	—	43	43	43	43	43
EPDM I	40	40	—	—	—	—
EPDM II	—	—	40	—	—	—
EPDM III	—	—	—	40	—	—
EPDM IV	—	—	—	—	40	—
EPDM V	—	—	—	—	—	40
Carbon black N 330	20	20	20	20	20	20

Carbon black N 762	60	60	60	60	60	60
ZnO	5	5	5	5	5	5
Ether thioether	10	10	10	10	10	10
Alkylsulfonic acid alkylphenyl ester	10	10	10	10	10	10
Styrolized diphenylamine	2	2	2	2	2	2
Zinc salt of 4- or 5- methylmercaptobenzthiazole	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1
CA stearate	1	1	1	1	1	1
Sulfur	1.8	1.8	1.8	1.8	1.8	1.8
Benzothiazyl-2-cyclohexyl sulfonamide	1.2	1.2	1.2	1.2	1.2	1.2

EPDM II contains 6 wt% 5-ethylidene-2-norbornene and 48 wt% ethylene and has a Mooney viscosity ML 1+4/100°C of 70 MU. /9

EPDM III corresponds to EPDM II, but the Mooney value is 110 MU.

EPDM IV contains 6 wt% 5-ethylidene-2-norbornene and 67 wt% ethylene and has a Mooney value of 85 MU.

EPDM V contains 11 wt% 5-ethylidene-2-norbornene and 45 wt% ethylene and has a Mooney value of 90 MU.

NBR IV has an acrylonitrile content of 39 wt% and a Mooney viscosity ML 1+4/100°C of 65 MU.

	1	2	3	4	5	6
Density (g/cm ³)	1.204	1.202	1.203	1.200	1.208	1.204
Blend ML 1+4/100°C/	54	60	69	82	76	75
Vulkameter 160°C						
t ₁₀	3.0	2.9	2.9	2.8	2.7	2.8
t ₉₀	16.6	15.3	15.5	14.9	14.8	18.5
Vulcanization 160°C	25 min	-----				
Tensile strength (MPa)	9.0	10.4	10.5	12.0	17.3	14.3
Breaking elongation (%)	170	170	175	190	280	230
Strain 100 % (MPa)	6.0	6.5	6.4	6.5	7.0	6.6
Hardness 23°C (Shore A)	72	72	72	74	78	73
Elasticity 23°C (%)	25	25	26	26	28	26

Long-term bending test, crack

formation Step 3

23°C (De Mattia), (no. of

bendings)

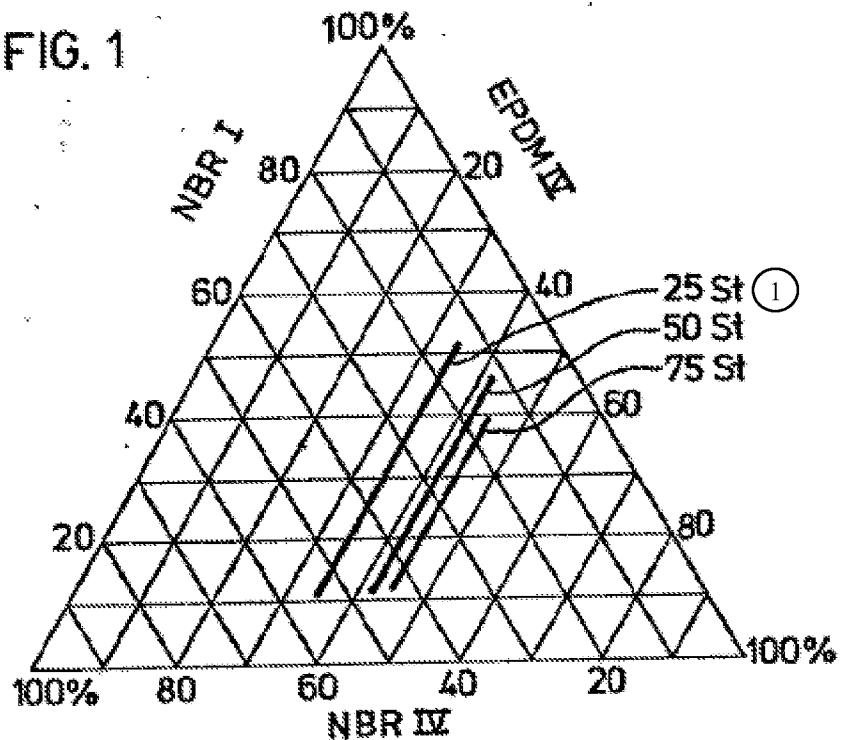
This example provides confirmation for the technically interesting compositions. The experiments were evaluated by means of a regression equation. The requirements on an NBR-EPDM blend can best be characterized by means of the following criteria:

- Good ozone resistance: largely determined by the EPDM content (Figure 1). Certain improvements can additionally be achieved through antiozonants and through the choice of the type of EPDM.
- Good mechanical properties, dynamic capability (for example, life span) and good low-temperature properties (for example, brittle point): these properties can be achieved only through the optimum choice and composition of the components in accordance with the invention (Figure 2).
- Sufficient resistance to swelling: here the phase structure and the average polarity (Figure 3) play a role (data in parts by weight).

	1	2	3	4	5	6	7	8	9
NBR I	31	10	17	3	17	24	10	17	24
NBR IV	34	60	38	62	48	46	50	58	36
EPDM IV	35	30	45	35	35	30	40	25	40
The formulation used is identical with that in Example 2									
Density (g/m ³)	1.20	1.21	1.19	1.21	1.21	1.20	1.20	1.21	1.20
Blend ML 1+4/100°C (MU)	65	67	74	68	66	66	70	63	69
Vulkameter 160°C									
T ₁₀	2.3	2.2	2.2	2.2	2.2	2.2	2.2	2.3	2.6
T ₉₀	11.3	13.5	13.1	14.2	13.5	12.6	14.3	14.2	13.0
Vulkameter 160°C 25 min.									
Tensile strength (MPa)	18.0	17.5	16.5	17.2	17.5	17.7	18.1	17.5	16.4
Breaking elongation (%)	323	262	290	281	310	307	309	315	283
100% strain (MPa)	5.1	6.2	5.9	6.2	5.7	5.8	6.0	5.2	6.1
Hardness 23°C (Shore A)	74	74	76	75	73	74	74	72	74
Elasticity 23°C (%)	34	30	33	29	31	32	31	29	33
Brittle point (°C)	-38	-36	-36	-28	-34	-40	-34	-34	-42
Ozone resistance, beginning of cracking, 1000 pphm, relative humidity 45%, 23°C									
30% elongation (h)	24	6	96	8	8	<4	12	<1	24

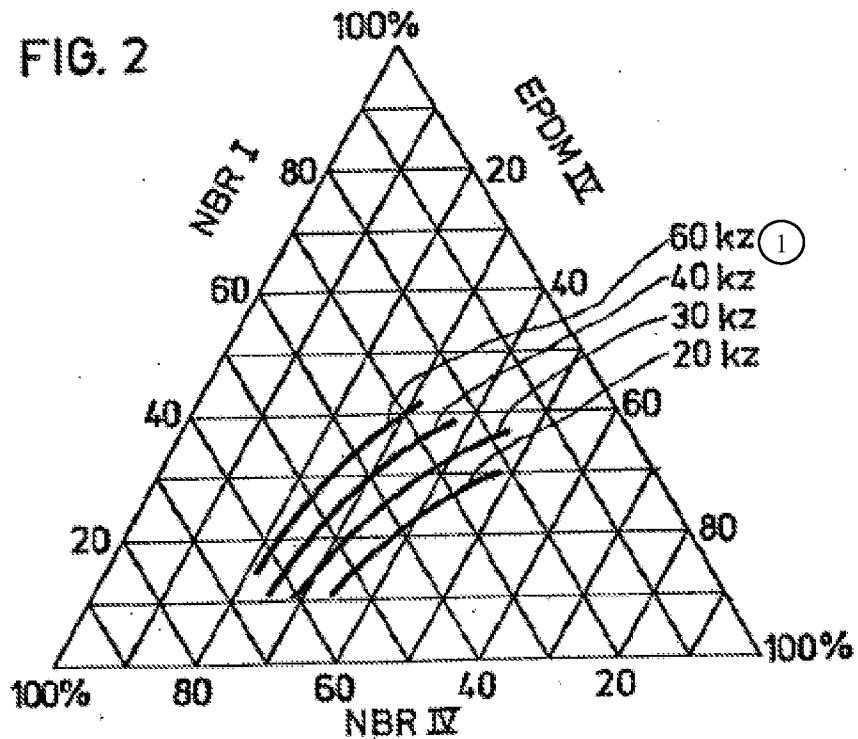
	1	2	3	4	5	6	7	8	9
Swelling in fuel Fuel 3, 48 h, 50°C									
ΔG (%)	66	47	66	49	57	54	57	46	67
ΔV (%)	105	75	104	78	90	85	90	73	111
Long-term bending test, crack formation, step 3 at 23°C (De Mattia)									
N (No. of bendings)	41	29	4	14	11	46	13	42	17

FIG. 1



Key: 1 h

FIG. 2



Key: 1 No. of bendings

FIG. 3

